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ELECTRONIC ABSORPTION SPECTRA OF ANION RADICALS OF DIPHENYL SULFONE AND DIBENZOTHIOPHENE-S,S-DIOXIDE

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The anion radicals of diphenyl sulfone and dibenzothiophene-S,S-dioxide produced by γ-irradiation showed intense absorption bands at 1030 nm and 850 nm, respectively. These absorption bands were assigned to the charge resonance bands from the energy diagrams including d-orbitals on sulfone groups, and the delocalization of an added electron on both phenyl rings was confirmed.

The anion radicals of diphenyl sulfone and dibenzothiophene-S,S-dioxide (DBT-S,S-dioxide) gave similar ESR spectra to that of the biphenyl anion radical and it was revealed that an added electron delocated on both phenyl rings.[1] These through conjugative effects of the sulfone groups are considered to be caused by the participations of d-orbitals. On the other hand, Ishitani and Nagakura reported that in the study of the biphenyl anion radical, new absorption band having the charge resonance character appeared in longer wavelength region than the absorption band of the benzene anion radical.[2] Then, it may be expected that, if the anion radical containing sulfone group was delocalized one, a new absorption band due to charge resonance should appear in longer wavelength region.

The anion radicals were produced by γ-irradiation of the sulfone compounds in 2-methyltetrahydrofuran (MTHF) at 77°K, and the absorption spectra were measured by a Cary 14 spectrophotometer at the same temperature. The blue glassy solution of γ-irradiated diphenyl sulfone exhibited the absorption bands at 1030 nm and 360 nm (Fig. 1-1). Although x-irradiation of the crystalline diphenyl sulfone gave the benzene sulfonyl radical,[3] the absorption spectrum of benzene sulfonyl radical formed by UV-irradiation of diphenyl disulfone solution at 77°K showed only a peak at 382 nm.[4] Another possible species in the blue solution may be solvated electron, which shows an absorption

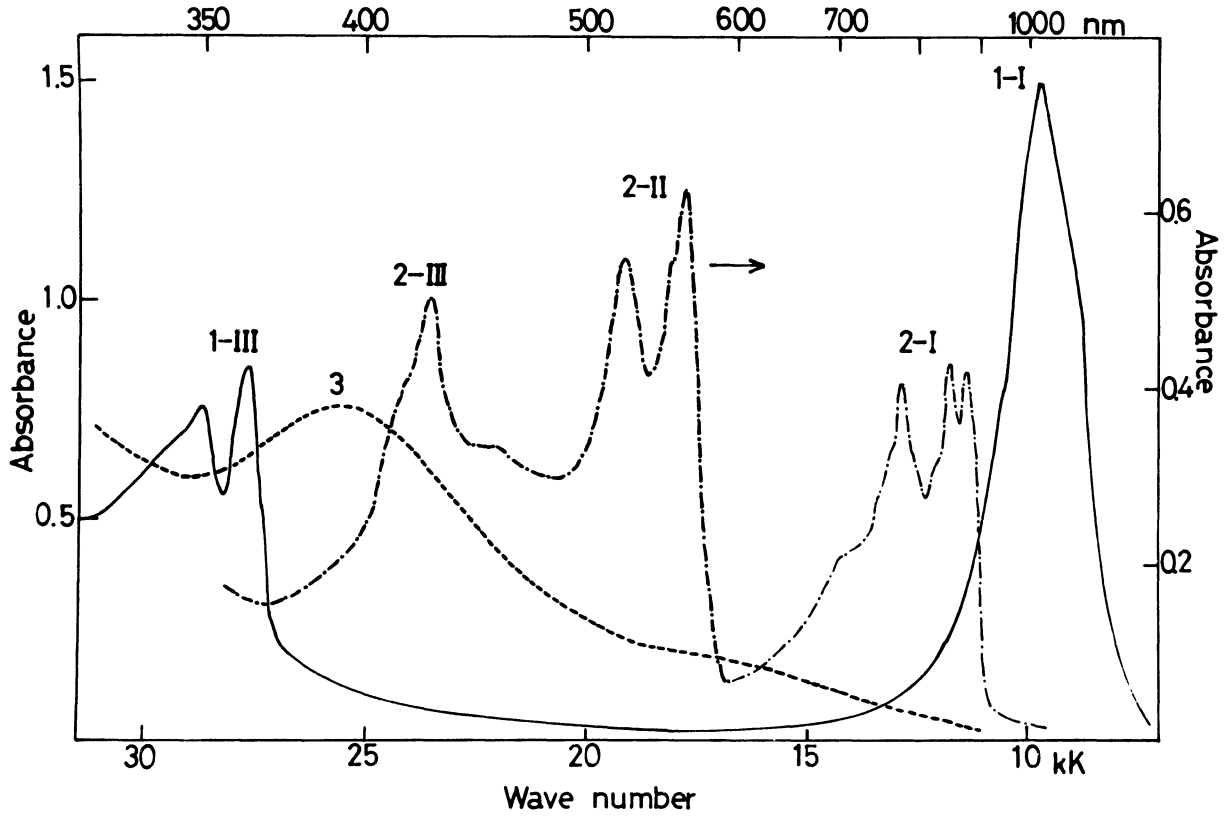

Fig. 1. Absorption spectra of (1) diphenyl sulfone, (2) dibenzothiophene-S,S-dioxide and (3) phenyl methyl sulfone anion radicals measured at 77°K (ca. 3 x 10^{-3} mol/l, 2 mm cell).

peak at 1200 nm (8.3 kK) and its band width is 5 kK.[5] While, blue species of diphenyl sulfone had a band at 1030 nm (9.7 kK) and its band width was 2 kK. Then, the absorption bands of the blue species of diphenyl sulfone shown in Fig. 1-1 can be safely assigned to its anion radical. The γ-irradiated DBT-S,S-dioxide showed three absorption bands in the region of 950 - 400 nm and each band had the vibronic structures as shown in Fig. 1-2. On the other hand, the γ-irradiated phenyl methyl sulfone showed an absorption band at 385 nm (Fig. 1-3). It was confirmed that phenyl methyl sulfone and phenyl sulfonyl chloride did not give the benzene sulfonyl radical by dissociative electron attachment by γ-irradiation in glassy solution. Furthermore, when the substituents such as CH_3O- and NO_2- were introduced on phenyl ring, the absorption peaks of the anion radicals (Y-  -SO_2-X) did not shift appreciably.[4] This indicates that an added electron locates on sulfone group in the phenyl methyl sulfone anion radical. Then, the appearance of the absorption bands in 1030 - 800 nm of the diphenyl sulfone and DBT-S, S-dioxide anion radicals may suggest that an unpaired electron delocates on two phenyl

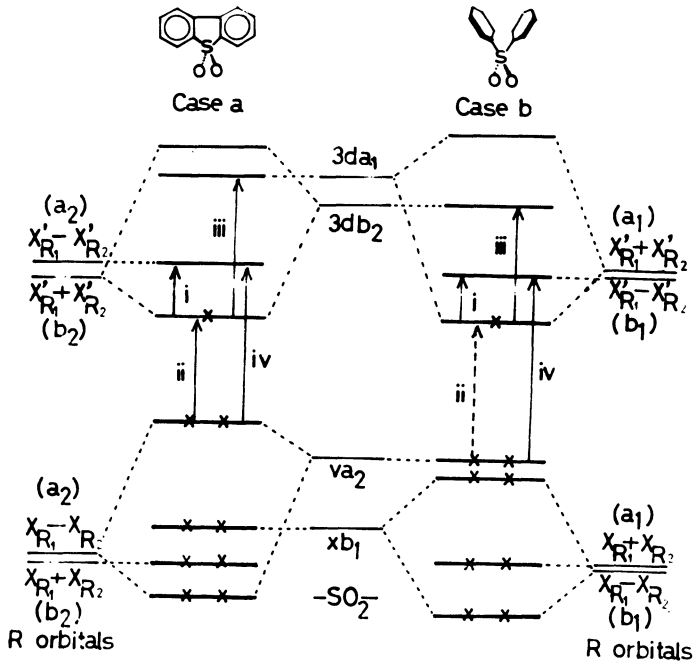

Fig. 2. Energy diagrams of the sulfone containing anion radicals. (R_1 and R_2 indicate the occupied π-molecular orbitals of phenyl rings 1 and 2, respectively, and R_1 and R_2 are those of vacant orbitals.)

rings.

According to Koch and Moffitt's classification, DBT-S,S-dioxide belongs to Case a, in which two phenyl rings and C_α-S-C_α are planar, and diphenyl sulfone belongs to Case b, in which two phenyl rings are perpendicular to the plane of C_α-S-C_α.[6] To explain the ESR data, Gerdil and Lucken gave the energy diagrams including d-orbitals for both cases by the qualitative considerations.[7] The energy diagrams given by Gerdil and Lucken are reproduced in Fig. 2.[7]

In Case a (DBT-S,S-dioxide) and Case b (diphenyl sulfone), the transition i in Fig. 2 is allowed by the Laporte selection rule and has a charge resonance character, $(X'_{R_1} \pm X'_{R_2}) \leftarrow (X'_{R_1} \mp X'_{R_2})$. The transitions at 1030 nm of diphenyl sulfone anion radical and at 850 nm of DBT-S,S-dioxide anion radical can be safely assigned to this type of transition. Splitting between $(X'_{R_1} + X'_{R_2})$ and $(X'_{R_1} - X'_{R_2})$ was caused by the interactions between d-orbitals on the sulfone group and π-orbitals on adjacent phenyl rings. This indicates that there is a strong conjugative interaction through the sulfone group between two phenyl rings of the anion radical. The absorption spectrum of the DBT-S,S-dioxide anion radical is rather similar to those of the anthracene and dibenzothiophene anion radicals, since this radical has a C-C bond connecting between two phenyl rings.

The transition ii of Case b is forbidden by the Laporte selection rule, and the diphenyl sulfone anion radical has no absorption band around 800 - 400 nm. While, since

the transition ii of Case a ($A_2 \leftarrow B_2$) is allowed, the absorption band at 550 nm of the DBT-S,S-dioxide anion radical can be attributed to this transition by the comparison of two spectra in Figs. 1-1 and 1-2. Since the transitions iii and iv in Case a are out of plane and short axis polarization, respectively, and these transitions in Case b are short axis polarizations, the relatively weak absorption bands at 450 nm of Case a and at 360 nm of Case b may be assigned to the bands arised from one of the transitions iii and iv.

On the bases of the group theoretical considerations, the absorption spectra of the diphenyl sulfone and DBT-S,S-dioxide anion radicals were reasonably assigned by the energy diagrams including d-orbitals presented by Gerdil and Lucken. It is concluded that the appearance of charge resonance band at longer wavelength region indicated the delocalization of an unpaired electron on both phenyl rings, and that the through conjugative effect is caused by the interactions between sulfone d-orbitals and adjacent π-orbitals on the phenyl rings. In the case of ESR studies, however, since only the lowest unoccupied molecular orbital was considered, the experimental spin densities were well reproduced not only by the simple Hückel molecular orbital calculations varying the parameters on the sulfone group, but also by a model considering the inductive effect of the sulfone group.[8] Then, to clarify the d-orbital participation for the through conjugative effect of sulfone group, it may be necessary to study these absorption spectra by more quantitative calculations including d-orbitals explicity.

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